A laboratory technique for the evaluation of electrochemical transparent conductive oxide delamination from glass substrates

K.W. Jansen*, A.E. Delahoy

Energy Photovoltaics, Inc., P.O. Box 7456, Princeton, NJ 08543, USA

Abstract

A rapid laboratory technique has been developed to evaluate the susceptibility of the transparent conductive oxide (TCO) layer to delaminate from its glass substrate in a thin film PV module. The test sample is stressed through the use of heat, humidity, and a DC bias to drive sodium ions to the TCO–glass interface. Delamination reactions occur at the interface causing the TCO to lose adhesion. The technique takes less than 15 min to complete and is useful in predicting the propensity of a thin film module to fail via electrochemical delamination of the TCO. Potential mechanisms for the adhesion failure are discussed.
© 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

As the use of thin film PV modules becomes more widespread, there is increasing focus on long-term module reliability. While there are several possible causes for thin film module failure in the field, one area of recent concern has been the electrochemical delamination of the transparent conductive oxide (TCO) layer from the soda-lime glass substrate. This is commonly caused by a combination of moisture ingress through the module encapsulation and an electrochemical reaction at the TCO–glass interface. While there has been extensive work to develop better encapsulation systems, there have been relatively few diagnostic tools to understand the degradation occurring at the TCO–glass interface. In this work, we describe a simple technique that is useful to the manufacturer of thin film PV modules to evaluate the integrity of this critical interface.

The earliest methods of evaluating the integrity of the TCO adhesion involved fabricating fully encapsulated modules and placing them in outdoor arrays. Early modules often showed signs of severe corrosion and TCO delamination due to the relatively poor encapsulation systems used [1].

The failures in these outdoor arrays led to the development of a variety of accelerated tests designed to reproduce the delamination under controlled laboratory conditions. Significant work was carried out at the Jet Propulsion Laboratory (JPL) to develop an accelerated electrochemical corrosion test. Researchers there placed a test module in a controlled atmosphere chamber at 85 °C and 85% relative humidity with 500 V applied between the metal frame and the shorted output leads and observed ionic electrochemical corrosion [2]. More recently, researchers at the National Renewable Energy Laboratory (NREL) have built upon the JPL work and have identified many of the key factors responsible for the electrochemical corrosion of SnO_2:F TCO films [3]. Both the JPL and NREL work acknowledged the need for a humid environment, elevated temperature, and a voltage bias between the module frame and the thin film device to cause thin film module corrosion.

The test methods developed in the laboratory and outdoors have proven to be very effective tools in the evaluation of finished encapsulated PV module reliability. However, for the manufacturer of PV modules, a more rapid test is required to manage product quality and reliability. A manufacturer is often faced with

---

*Corresponding author. Tel.: +1-609-587-3000; fax: +1-609-587-5355.

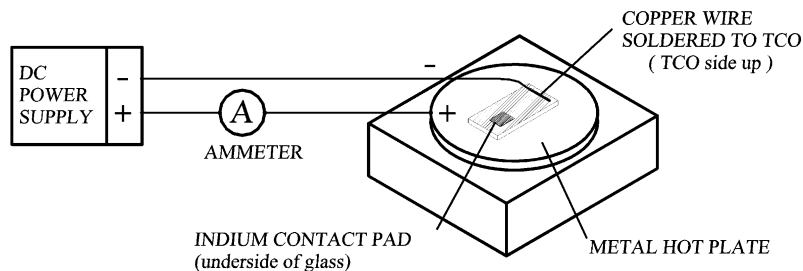*E-mail address:* k.jansen@epv.net (K.W. Jansen).

Fig. 1. Test apparatus showing indium contact on the test sample and connections to the electrically isolated DC power supply.

process variation in their TCO supply that must be must be evaluated and screened to ensure that modules fabricated from a given source of TCO will not be prone to delamination in the field. Thus, for thin film PV module manufacturers, there are two major disadvantages in relying on the existing tests:

1. The tests require a completed encapsulated module to undergo testing. This significantly delays the feedback of the TCO quality to the manufacturer and requires them to add significant value to the TCO substrate undergoing test.
2. The tests are time consuming. Typically, the tests run anywhere from several days to several weeks. In this time frame, a manufacturer could produce a considerable amount of product and could be at considerable risk of producing modules that are susceptible to electrochemical delamination and failure in the field.

Consequently, a manufacturer needs a rapid reliable test technique to minimize delay, maintain high quality and minimize risk.

To address this need, we have developed a rapid test to quantify the susceptibility of a TCO substrate to undergo delamination. The key features of our test are:

1. It is fast. It takes as little as 15 min to determine if there is a TCO quality problem.
2. It requires no specialized equipment. All of the equipment is found in a typical PV module development facility.
3. It tests the key point of failure, the TCO, prior to subsequent processing steps. This eliminates adding value to a substrate that is likely to fail in later environmental tests.
4. It requires only a small TCO sample. Typically a sample is approximately 10 cm^2.
5. The test is repeatable and reliable.

2. Laboratory test technique

The laboratory technique involves heating a small sample of TCO coated glass and passing current through it as described below:

1. A small sample of TCO coated soda-lime glass is cut to a small convenient size. For most of the work described here, the TCO was SnO_2:F and the samples were cut to approximately 2×5 cm.
2. A copper contact wire is soldered to the TCO on one end of the sample as shown in Fig. 1.
3. Electrical contact to the glass is made via an indium contact pad, approximately 1×1 cm, soldered to the glass side of the sample as shown in Fig. 1.
4. The sample is placed glass side down on a heat source that has an electrically conductive surface, such as a pre-heated metal hot plate. The electrically conductive surface contacts the indium contact pad on the glass side of the sample to provide a convenient electrical connection.
5. The sample then heats rapidly to approximately 180–225 °C, or higher as desired. As the sample heats, the indium contact pad melts and helps heat sink the glass to the hot plate.
6. The wire soldered to the TCO is connected to the negative side of an electrically isolated DC power supply, and the electrically conductive hot plate, which is contacting the glass side of the sample, is connected to the positive side of the power supply, as shown in Fig. 1. An ammeter is installed in series with the sample to monitor the current flow.
7. A bias of 10–100 VDC is applied to the sample for approximately 3–15 min and the sample is removed from the power supply and heat source. The sample is allowed to cool in a mildly humid environment, typically 40–60% relative humidity, and the sample is observed for signs of TCO delamination.

As the sample cools, it reacts with the humidity in the air and may begin to delaminate, depending upon its propensity to do so. The delamination can begin in as short as a few seconds to as long as a few days, depending upon the sample, the applied voltage, the processing temperature, and the humidity.

An example of a sample that has been processed using this rapid delamination technique is shown in Fig. 2. This figure shows the delamination of a sample of SnO_2:F that was treated at 100 VDC for 15 min at 225 °C. The sample was fully intact immediately after
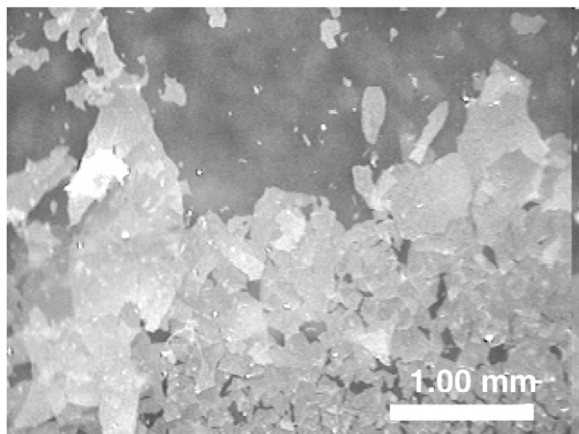
Fig. 2. Micrograph of SnO$_2$:F coated soda-lime glass after treatment showing delamination of the TCO.

removal from the power supply and heat source, and it delaminated in less than 2 min, upon cooling and exposure to the humidity of the ambient air.

## 3. Results and discussion

3.1. Proposed mechanism

This technique is based on the forced migration of cations through the glass substrate and subsequent delamination reactions occurring at the TCO–glass interface. This is the same general mechanism described by the NREL researchers for the electrochemical delamination of TCO in thin film modules [3].

It is well documented that monovalent cations are the most mobile species in glass and that of these, the sodium ion, Na$^+$, is the most mobile [4]. It is also well known that the mobility of Na$^+$ increases with increasing temperature and that an applied voltage across the thickness of a glass substrate will drive cations toward the cathode (negatively biased surface) [5]. Thus, in the first part of our technique, we exploit these phenomena by intentionally driving the Na$^+$ ions to the TCO–glass interface by heating the TCO sample and then applying a negative bias to the TCO with respect to the glass.

The migration of Na$^+$ and subsequent build-up of charge at the interface has been verified experimentally. TCO samples that have been biased at 100 V for 15 min at 180 °C and then removed from the power supply and heat source has been measured to show a clear charge separation through the thickness of the substrate. The Na$^+$ ion build-up at the interface results in a measurable voltage of 1–3 V at very low currents at 25–100 °C, depending upon the amount of Na$^+$ that has been driven from the glass to the interface. The charge separation can easily be measured with an electrometer having a very high input impedance (greater than ~10^{12} Ω). The ability to measure this charge

separation is an interesting phenomenon that is likely to have practical application, but is not currently part of our screening technique.

As Na$^+$ ions migrate toward the TCO–glass interface and accumulate, some of the Na$^+$ ions at the interface become reduced to Na as they come into contact with the electrons at the cathode according to the well-known sodium reduction reaction:

$$Na^+ + e^- \leftrightarrows Na$$
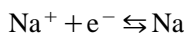
This has been observed experimentally during the bias treatment of both SnO$_2$:F and ZnO samples as a darkening of the TCO films.

In the second part of our technique, the sample is removed from the heat source and electric field, and is allowed to cool to room temperature in a mildly humid room, approximately 40–60% relative humidity. While the sample is cooling, water vapor from the room is able to diffuse to the TCO–glass interface. This presumably occurs through the grain boundaries of the TCO, although we have not yet investigated the exact manner in which this takes place. When the water reaches the sodium enriched TCO-glass interface, a series of delamination reactions take place that cause the TCO bonds to break resulting in the loss of adhesion to the substrate.

Although the precise delamination reaction mechanism is not fully known, a reasonable mechanism can be inferred based on the experimental observations. It is reasonable that the darkened layer of elemental sodium formed during the biasing treatment reacts with the diffused moisture from the atmosphere at the TCO-glass interface. This results in the generation of atomic hydrogen, a known TCO reducing agent. The atomic hydrogen acts to reduce the TCO and break the metal–oxygen bonds adhering the TCO to the SiO$_2$ based substrate surface. In the case of a SnO$_2$ based TCO, the reactions can be described as follows:

1. Sodium is reduced and elemental hydrogen is formed.

$$H_2O + Na \rightarrow NaOH + H$$
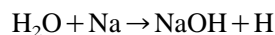
2. Tin oxide is reduced and hydrogen is oxidized, forming water that can further react with more sodium. The tin–oxygen bond adhering the TCO to the glass substrate is broken.

$$4H + SnO_2 \rightarrow Sn + 2H_2O$$
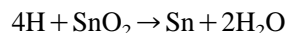
In the highly reducing environment at the TCO–glass interface, it is also possible that sodium hydride might be generated as an intermediate species. If so, then the reduction of the tin oxide could occur through reaction with the hydride intermediate as described by:

$$2NaH + SnO_2 \rightarrow Sn + 2NaOH$$
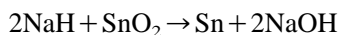
In addition to the above oxidation–reduction reactions, other reactions occur at the interface to further

disrupt the adhesion of the TCO. One of these is the classical Stage 1 glass corrosion reaction. In Stage 1 glass corrosion, water rapidly reacts with sodium ions in the glass to form NaOH while driving hydrogen ions from the water into the glass matrix to maintain charge equilibrium in the glass [6]. This can be described according to the following reaction:

$$\text{SiONa (glass matrix)} + H_2O \text{ (solution)}$$
$$\leftrightarrows \text{SiOH (glass)} + \text{NaOH (solution)}$$
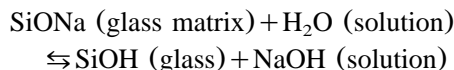
With a relatively high concentration of sodium ions at the TCO–glass interface as a result of the biasing treatment, it is expected that this reaction occurs at a sufficiently high percentage of the surface sites to further compromise the adhesion of the TCO to the glass by facilitating the sodium migration from the glass.

Another possibility for the delamination of fluorinated TCO compounds such as SnO_2:F is via the formation of hydrofluoric acid at the interface, which attacks the silicon–oxygen bonds adhering the TCO to the glass. A similar mechanism to this has been demonstrated to cause adhesion problems on silicon dioxide coated silicon wafers that have trace amounts of fluorine contamination [7]. This etching process could occur as follows:

1. Fluorine in the TCO film combines with moisture at the interface to form hydrofluoric acid.

$$F^-\text{(in } SnO_2 \text{ matrix)} + H_2O \rightarrow HF + OH^-$$
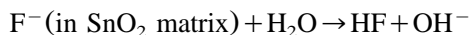
2. The HF attacks the silicon–oxygen bond and breaks up the glass matrix by fluorinating a silicon atom and leaving a stable SiOH bond on the adjacent silicon.

$$HF + \ldots O-Si-O-Si-O-Si\ldots \text{(glass matrix)}$$
$$\rightarrow \ldots O-Si-OH + F-Si-O-Si\ldots$$
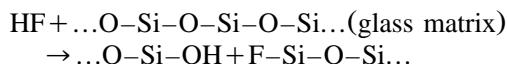
3. Additional moisture can react with the fluorinated silicon to form another stable SiOH bond and HF, which allows the process to perpetuate.

$$H_2O + F-Si-O-Si\ldots \rightarrow HO-Si-O-Si\ldots + HF$$
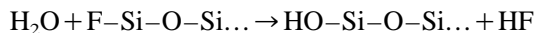
Finally, it should be mentioned that the simple physical accumulation of sodium at the TCO–glass interface resulting from the bias treatment adds to the stress of the TCO film and further promotes delamination. It is evident from the experimental observations that the physical accumulation of the migrated sodium is not sufficient on its own to delaminate the TCO. If it were, the delamination of the TCO would occur during the biasing phase of the treatment and well before moisture could diffuse to the interface and react. However, it is reasonable to conclude that the physical presence of a relatively high concentration of sodium can cause increased mechanical stress at the interface that can facilitate the delamination process propagated by the reactions described above.
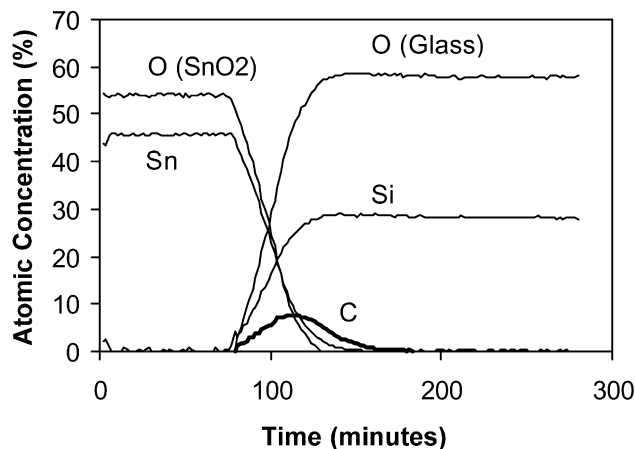

Fig. 3. XPS depth profile of a standard SnO_2:F TCO substrate.

After the adhesion of the TCO is compromised through one or more of these mechanisms, the accumulated stress from the ion migration and the inherent stress in the film causes the TCO to crack. If there is sufficient stress and the TCO adhesion is low enough, the TCO will lift off of the glass substrate and crack into small pieces ranging from several microns to several millimeters in size. An example of a severely stressed SnO_2:F TCO substrate is shown in Fig. 2.

3.2. Analysis of the delaminated surface

In order to determine in which layer the TCO delaminated from the glass substrate, X-ray photoelectron spectroscopy (XPS) was used to analyze a SnO_2:F surface that had been delaminated using this technique. The untreated SnO_2:F TCO is comprised of three chemically distinct layers: (1) the bulk soda-lime glass substrate, (2) a silica barrier layer that contains carbon, and (3) the conductive tin oxide layer.

Fig. 3 shows the XPS sputtered depth profile of a standard SnO_2:F TCO with these three distinct layers present. The tin oxide layer is clearly identifiable on the left as tin and oxygen signals, while the glass substrate is clearly visible on the right as silicon and oxygen signals. Between these two layers, in the transition region, the silica barrier layer is visible as evidenced by the carbon peak.

Fig. 4 shows the XPS depth profile for the delaminated substrate. A careful look at the carbon signal will show that it starts at ~20 at.% at the sample surface and quickly falls to ~10% where it persists for quite some time before dropping off again. While the initial fall from ~20 to ~10% is likely due to surface contamination, the persistence of the carbon signal at ~10% indicates that the barrier layer is still present on the delaminated sample, and thus the delamination occurred at the TCO-barrier layer interface. This is also
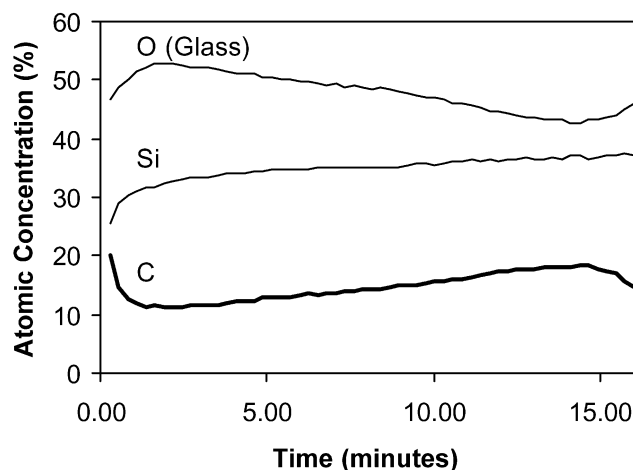
Fig. 4. XPS analysis of the surface of a delaminated SnO$_2$:F TCO substrate.

Fig. 5. Micrograph of a ZnO film after treatment showing extensive cracking of the TCO.

supported by other XPS analyses that indicate that the silicon at the surface of a delaminated sample has the same bonding energy as silicon from the barrier layer, which is different from the silicon in the bulk glass. The delamination of the TCO from the barrier layer is consistent with our delamination model that describes the breaking of tin–oxygen bonds at the TCO–glass interface, the carbon containing silica layer representing the glass in this TCO structure.

3.3. Effect of treatment on zinc oxide

Since most of our work was performed on SnO$_2$:F, we decided to test the technique on a zinc oxide coated glass sample to determine if the delamination effects we observed were confined to tin oxide based TCO. A sample of soda-lime glass was coated with sputtered zinc oxide and subjected to the same delamination treatment described previously. After the bias was applied, it was noted that the film had darkened just as the SnO$_2$:F based TCO had. This provided further evidence that the darkening was the result of sodium and not TCO reduction, since ZnO is reported to be largely immune to reduction by atomic hydrogen [8]. After cooling in humid air, the zinc oxide film cracked extensively, as shown in Fig. 5, which indicates that the damage to the TCO is not dependent upon the presence of SnO$_2$:F. Presumably, the reaction mechanisms for the bias effects of these films are analogous.
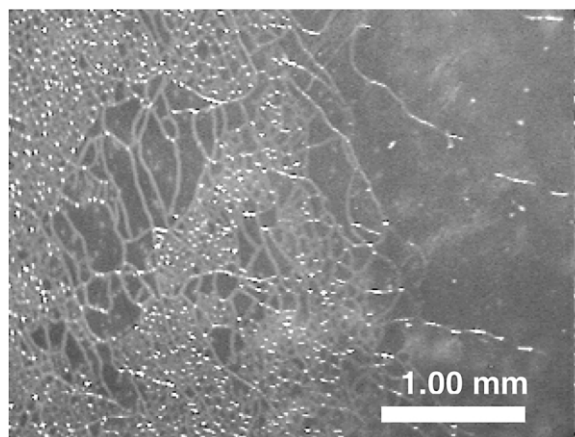
One significant difference between the cracking of the ZnO in Fig. 5 compared to the SnO$_2$:F delamination in Fig. 2 is that while the ZnO film appeared to shatter after processing, the SnO$_2$:F film appeared to shatter and peel up from the substrate as a result of the treatment. This appears to be an indication that the sputtered ZnO film has lower film stress than the SnO$_2$:F film deposited by APCVD. This is reasonable since the sputtered ZnO was deposited close to room temperature and therefore has very little thermally induced stress. The SnO$_2$:F film was deposited above 550 °C and then cooled to room temperature. This contributes to significant stress in the film arising from the difference in the thermal coefficients of expansion between the glass and the SnO$_2$:F.

3.4. Reversibility of bias effects

In our experiments, we have found that up to the point of TCO film delamination, the bias effects on a TCO substrate are completely reversible. To demonstrate this phenomenon, samples of SnO$_2$:F and ZnO were bias treated using the process previously described and the changes in the appearance of the samples were noted. Prior to cooling the samples and allowing moisture to diffuse to the TCO-glass interface, the samples were subsequently biased with the opposite polarity to drive cations away from the interface in an attempt to reverse the bias effects. The results are shown in Table 1.

Table 1
Reversibility of bias effects

TCO Type	After −100 VDC on TCO	After −100 V then +100 VDC on TCO	After exposure to humid air
SnO$_2$:F	Darkened film	Transparent film	No delamination
ZnO	Darkened film	Transparent film	No delamination

It is apparent from this experiment that when both SnO$_2$:F and ZnO are biased in the normal fashion, the TCO is darkened, presumably by the sodium reduction method mentioned previously. However, when the polarity of the bias is then reversed, the darkening of the films reverses as the film reverts to its original state. Subsequent exposure to moisture in the air results in no film delamination. This is consistent with the delamination model proposed involving the reduction of Na$^+$ to Na. As sodium metal is formed from the ion, it darkens the film, but when the bias is reversed, the Na reverts back to Na$^+$ and the optical transmission of the film is restored.

3.5. Effect of water vapor

To test the effect of the presence of water vapor on the TCO samples, we biased three SnO$_2$:F samples as per our standard technique. It was noted that after the bias treatment, all three samples darkened as expected. After the bias treatment was complete and while the samples were still hot, we immediately placed two of them in dry environments. One of these samples was placed in a vacuum chamber and the other sample was placed in a sealed container that contained an anhydrous calcium sulfate desiccant. The control sample was left out in the humid room to delaminate.

As shown in Table 2, the control sample delaminated in approximately 1 min, while both samples that were stored in dry environments were still intact after 2 days. Upon removal from their dry environments, the samples that were intact when dry began to delaminate when exposed to humid air. These results clearly show that in the absence of moisture, the delamination reactions do not occur. It is also clear that the effects of the biasing treatment are able to lie dormant in the TCO for quite some time as long as moisture is not introduced to the TCO. Upon exposure to moisture, the delamination reactions occur and irreversible damage to the TCO proceeds.

3.6. Temperature dependence of ion migration

The temperature dependence of the treatment process at 100 V was characterized and the results are shown in

Fig. 6. Arrhenius plot of ln(current) vs. inverse temperature for a sample processed at 100 VDC.

Fig. 6 as an Arrhenius plot. The graph shows a fairly linear relationship between ln(current), and inverse temperature, and clearly demonstrates that the process is thermally activated. The activation energy of this process is found to be 0.79 eV, which is in good agreement with the 0.78 eV activation energy identified by the NREL researchers working on completed modules [3].

3.7. Effect of sodium in the glass substrate

In order to test the effect of sodium content in the substrate on the delamination process, we processed a piece of tin oxide coated borosilicate glass using our technique. The borosilicate glass has approximately 25% of the sodium of standard soda-lime glass. As expected, the lower concentration of Na$^+$ ions in the glass significantly reduced the amount of current passed through the glass during processing. After processing, there was no cracking or delamination of the TCO. Thus, it appears that the sodium content of the substrate is a significant factor in the delamination process. This result is consistent with the mechanism described above, in which the Na$^+$ ions are necessary to react at the TCO-glass interface to cause delamination. Glasses with lower Na$^+$ concentrations experience much less damage than glasses with higher Na$^+$ concentration.

Table 2
Effect of moisture on bias treated SnO$_2$:F TCO

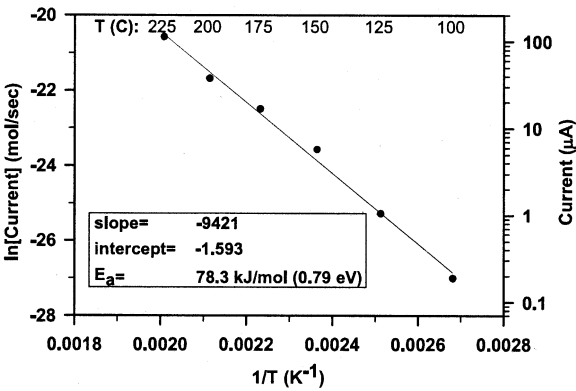| Storage atmosphere for treated sample	Observations—in storage	After removal from storage and exposed to humid air
Humid room air	Delaminates in ∼1 min	N/A
Vacuum chamber with roughing pump	No delamination after 2 days	Delaminates in 10 min
Sealed container with CaSO$_4$ desiccant	No delamination after 2 days	Delaminates in 10 min

Table 3
Comparison of rapid TCO delamination technique with delamination of TCO in modules

Sample	Applied voltage (V)	Temperature (°C)	Treatment duration (min)	Time to delaminate after treatment	Module delamination
A	100	185	15	No delamination	No
	20	185	15	No delamination	
	100	225	30	1 h	
B	100	185	15	No delamination	No
	20	185	15	No delamination	
C	100	185	15	No delamination	N/A
	20	185	15	No delamination	
D1	100	185	15	1.5 min	Yes
	20	185	15	9 min	
D2	100	185	15	1 min	Yes
	20	185	15	No delamination	
E	100	185	15	1 min	N/A
	20	185	15	23 h	

3.8. Correlation with TCO delamination in PV modules

In order to compare the results of our rapid TCO delamination test with TCO delamination observed in modules, samples of TCO were tested from batches of TCO that produced both severely delaminated modules and modules with no delamination. The results are shown in Table 3.

These data show that for the modules that had severe delamination, the rapid delamination test identified the weakness in the TCO in approximately 1 min after a 100 VDC bias was applied for 15 min at 185 °C. In addition, there was also good correlation between modules that did not delaminate and TCO that did not delaminate in our laboratory tests at 100 VDC for 15 min. We conclude that the 15 min, 100 VDC treatment at 185 °C works well as a screening tool to evaluate the susceptibility of a TCO substrate to delaminate when fabricated into a thin film PV module.

At the lower treatment voltage, one susceptible TCO sample delaminated, but another did not. This indicates that the lower treatment voltage is less reliable for use as a screening tool, but it is still quite capable of damaging the TCO in some samples. The data also show that the time necessary for delamination to occur increases at lower applied voltages. This is consistent with our model, since as the applied voltage is decreased, the current flow through the glass decreases and fewer Na$^+$ ions are driven to the TCO–glass interface and participate in the delamination reactions. This results in less damage to the interface and thus delamination takes longer to occur.

We have also found that when TCO that is not prone to delamination is treated at higher temperatures and longer durations at a high voltage, it can often be delaminated or damaged if the conditions are severe enough. An example of this is shown in Table 3. TCO 'A' is shown to be a fairly robust TCO that is able to withstand delamination treatments at both 20 and 100 VDC at 185 °C. In addition, modules made with this TCO typically have good resistance to delamination. However, when this TCO is subjected to a more severe treatment at 100 VDC at 225 °C for 30 min, it delaminates from the glass substrate in 1 hour. We have found this result to be typical for all of the soda-lime glass based TCO that we have tested. When large enough amounts of sodium are moved to the TCO–glass interface, and the subsequent delamination reactions proceed, it appears inevitable that all TCO becomes irreversibly damaged, based on our tests. Therefore, we have found that the selection of the treatment voltage, sample temperature, and treatment duration is critical to the development of a screening test that correlates well to the observed TCO delamination in modules. The treatment conditions for our rapid delamination test that we have found to correlate best are 100 VDC at 185 °C for 5–15 min.

4. Summary and conclusion

The laboratory technique described has been shown to provide a rapid evaluation of the susceptibility of a TCO substrate to undergo delamination. It is based on stressing the TCO by applying the key environmental factors of heat, humidity, and a DC bias on the TCO to drive sodium ions from the glass to the TCO–glass interface. For a TCO sample that is prone to delamination, the weakness of the TCO can be identified in less than 15 min. Several possible mechanisms could contribute to the adhesion failure at the TCO–glass interface including the physical accumulation of sodium, the reduction of the tin oxide, and the fluoride attack of the silicon–oxygen bonds at the interface. The technique is quick and easy enough to be used as part of an incoming quality assurance inspection, and it has demonstrated its

effectiveness as a screening tool to improve the long-term reliability of thin film PV modules.

Acknowledgments

References

[1] D.A. Fagnan, R.V. D'Aiello, J. Mongon, in: L.L. Kazmerski (Ed.), Proc. 19th IEEE Photovoltaic Specialists Conference (New Orleans), IEEE, Piscataway, 1987, pp. 1508–1509.

[2] G.R. Mon, R.G. Ross, Jr., in: A.M. Barnett (Ed.), Proc. 18th IEEE Photovoltaic Specialists Conference (Las Vegas), IEEE, Piscataway, 1985, pp. 1142–1149.

[3] C.R. Osterwald, T.J. McMahon, J.A. del Cueto, 'Electrochemical Corrosion of SnO_2:F Transparent Conducting Layers in Thin Film Photovoltaic Modules', Solar Energy Materials and Solar Cells, in press, 2002.

[4] R.H. Doremus, Glass Science, John Wiley and Sons, New York, 1994, p. 263.

[5] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Introduction to Ceramics, John Wiley and Sons, New York, 1976, pp. 875–876.

[6] P.F. Duffer, 'How to Prevent Glass Corrosion', Glass Digest, November 15, 1986.

[7] L.P. Buchwalter, R.H. Lacombe, J. Adhes. Sci. Technol. 2 (6) (1988) 463–482.

[8] K. Sato, Y. Matsui, K. Adachi, Y. Gotoh, Y Hayashi, H. Nishimura, in: R.J. Schwartz (Ed.), Proc. 23rd IEEE Photovoltaic Specialists Conference (Louisville), IEEE, Piscataway, 1993, pp. 855–859.